

- sites spanning a wide range of late Maastrichtian paleodepths (1 to 3.5 km) and paleolatitudes (36°N to 70°S). If these tests were in isotopic equilibrium with their paleoenvironments, the mean $\delta^{18}\text{O}_c$ value of benthic foraminifera from all 16 sites (0.51 per mil) approximates that of benthic foraminifera in equilibrium with mean late Maastrichtian deep water. Given a mean $\delta^{18}\text{O}_w$ value of -1.0 per mil for late Maastrichtian seawater (16), a mean benthic $\delta^{18}\text{O}_c$ value of 0.51 per mil indicates a mean deep-ocean paleotemperature of 10.2°C. Estimates of the mean $\delta^{18}\text{O}_w$ of Late Cretaceous seawater typically assume that there was no globally significant Late Cretaceous ice volume and that the mean $\delta^{18}\text{O}$ value of the terrestrial surface hydrosphere has not changed over the past 100 million years (16). The mean salinity of Late Cretaceous seawater can be similarly estimated. Given a lack of substantial ice volume and a constant salt balance in the surface hydrosphere, Late Cretaceous oceans were characterized by a mean salinity of ~ 34 psu. If the late Maastrichtian deep ocean was characterized by a mean temperature of 10.2°C and a mean salinity of 34 psu, its mean density was 1026.13 kg m $^{-3}$ [density equation is from F. J. Millero and A. Poisson, *Deep-Sea Res.* **28A**, 625 (1981)].
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5 October 1995; accepted 21 December 1995

Alpe Arami: A Peridotite Massif from Depths of More Than 300 Kilometers

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The abundance of FeTiO_3 and chromite precipitates in olivine of the Alpe Arami peridotite massif, Switzerland, requires a much higher solubility for highly charged cations than is found in mantle xenoliths from depths of 250 kilometers. Three previously unknown crystal structures of FeTiO_3 were identified that indicate that the originally exsolved phase was the high-pressure perovskite polymorph of ilmenite, implying a minimum depth of origin of 300 kilometers. These observations, coupled with the unique lattice preferred orientation of olivine, further suggest that the original composition of olivine may reflect that of a precursor phase, perhaps wadsleyite, that is stable only at depths greater than 400 kilometers.

In recent years, rocks have been discovered that were brought to Earth's surface by a poorly understood process that can accompany or follow subduction of shallow material to great depths. These bodies, some of which contain diamonds (1), provide a window into processes active at depth in subduction zones (2). Such rocks can potentially provide information about the composition and phase relations in the mantle wedge overlying subduction zones, and they may cast light on the problem of recycling of volatiles into the deep interior. We now report observations that suggest that the Alpe Arami peridotite massif, Switzerland, has come to the surface from depths of 400 to 670 km, the mantle transition zone.

The Alpe Arami massif, which yields consistent mineral ages of ~ 40 million years (3), is situated within Lepontine gneisses of the Ticinese root zone of the Pennine Alps. It consists of a small wedge of garnet lherzolite bordered by kyanite eclogite, all showing variable degrees of low-pressure hydrous alteration (4). The maximum pressure of metamorphism in the Lepontine nappe increases toward the south; the Alpe Arami massif, located near the southern margin, records the highest pressures, with garnet-orthopyroxene-clinopyroxene equilibration at approximately 1200 to 1300 K and 4 to 5 GPa (3, 5, 6). These

results establish a minimum depth of origin of 120 to 150 km.

Like most peridotite massifs, Alpe Arami has experienced considerable subsolidus deformation and partial recrystallization of olivine, with consequent development of foliation and lineation. The oldest generation of olivine consists of larger, plastically deformed, porphyroclasts that exhibit an unexplained pattern of lattice preferred orientation (LPO) that is different from that displayed by any other peridotite (4, 7) and is inconsistent with the crystal plasticity of olivine (8). This pattern must have formed by a different, unknown, mechanism.

We analyzed fresh peridotite that exhibited large (1 to 2 cm), deep red-violet garnets, which commonly displayed bright apple-green clinopyroxenes (1 to 3 mm), both as inclusions and as clusters around their margins (Fig. 1A). Similar textures have been reported from mantle xenoliths and were interpreted as evidence of an ultradeep (>300 km) origin (9). The garnets of Alpe Arami also exhibited abundant exsolved needles of rutile and small, oriented, euhedral-to-subhedral crystals of pargasite-edeneite amphibole, which were always accompanied by an orthopyroxene-spinel symplectite and were usually accompanied by magnetite, apatite, and an Fe-Ni sulfide (Fig. 1, B and C). These multiphase inclusions appear to represent a complex reaction between an originally exsolved phase, probably clinopyroxene (plus olivine?), and the host garnet during decompression of the massif.

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The composition of the two generations of olivine in the massif is approximately $(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$, but the abundances of trace elements in the two generations are distinctly different. As is typical for mantle olivine from all but the deepest (xenolith) environments (10), the concentration of foreign cations is extremely low in the younger, recrystallized, olivine. However, the concentrations of these elements in the older generation of olivine are in some cases much higher. For example, TiO_2 concentrations can approach 500 parts per million, which is comparable to the highest concentrations found in olivine of the deepest mantle xenoliths (10). Moreover, unlike olivine of all peridotites previously described in the literature, the relict porphyroclastic olivine of the garnet facies of Alpe Arami exhibits extensive exsolution of what originally appeared to be ilmenite, and of chromite (Fig. 2). These precipitates are present in all crystals of this older generation of olivine, which constitutes most of the olivine in the freshest rocks. They are also present in the abundant olivine inclusions in garnet and in rare olivine inclusions in orthopyroxene, but are absent in recrystallized olivine; oxides in the latter case are confined to grain boundaries.

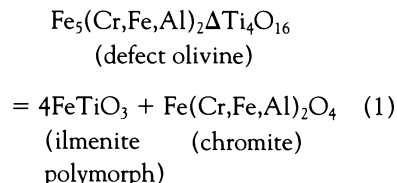
The most abundant inclusions are black-brown rods of FeTiO_3 , 2 to 20 μm long by 0.2 to 4 μm in diameter, oriented parallel to [010] of the olivine host (Fig. 2A). The inclusions constitute generally more than 1%, and locally as much as 3% by volume, of the olivine crystals. Chromite crystals are extremely thin, nearly transparent plates a few micrometers on a side and $\leq 0.5 \mu\text{m}$ thick. The plates lie in the (100) plane of the olivine host; they commonly are rectangular, with the longer dimension parallel to [010] of olivine and the shorter dimension parallel to [001]. They occur both as separate inclusions (Fig. 2B) and as composite inclusions with the FeTiO_3 rods; this finding suggests simultaneous precipitation or nucleation of one phase on the other (Fig. 2C). Semi-quantitative analysis of these phases (Fig. 2D) in the transmission electron microscope (TEM) showed strong Ti and Fe peaks and a weak Mg peak for the FeTiO_3 crystals; chromite exhibited strong Cr and Fe peaks with a weaker Al peak. The thinness and near transparency of the chromite impeded estimation of the composition and abundance of this phase, but the volume fraction seems to be only about one-fifth as large as that of the much more prominent "ilmenite."

Examination by TEM and selected area electron diffraction showed that the FeTiO_3 rods display at least four crystal structures, all of which have the same chemical composition. The phases range from a previously

unknown orthorhombic structure that is almost completely coherent with olivine (Fig. 3, A and B), through two structural intermediates (also previously unknown), to true ilmenite (Fig. 3C). In all cases, topotaxy is maintained with the olivine host. We will refer to the phase shown in Fig. 3, A and B, as $\beta\text{-FeTiO}_3$; its crystal axes are parallel to those of olivine, and its lattice parameters ($a = 0.470 \text{ nm}$, $b = 1.028 \text{ nm}$, $c = 0.574 \text{ nm}$) are almost identical to those of olivine ($a = 0.480 \text{ nm}$, $b = 1.028 \text{ nm}$, $c = 0.603 \text{ nm}$). The topotaxy between olivine and ilmenite (Fig. 3C) is $[0001]_{\text{il}}/[100]_{\text{ol}}$; $[1120]_{\text{il}}/[010]_{\text{ol}}$; $[0110]_{\text{il}}/[001]_{\text{ol}}$. The chromite plates all show $[111]_{\text{chr}}/[100]_{\text{ol}}$; $[1\bar{2}1]_{\text{chr}}/[010]_{\text{ol}}$; $[10\bar{1}]_{\text{chr}}/[001]_{\text{ol}}$.

Crystallographically oriented ilmenite and spinels (including chromite) have been reported in olivine, but in every case the crystals were smaller and less abundant (11–13). In these earlier studies, both kinds of inclusions occurred as thin flakes lying in (100) of olivine, with topotaxy reflecting minimal rearrangement of the hexagonal close-packed (hcp) layers of the oxygen sublattice—the same topotactic relations we found, although not the same morphology for ilmenite and the other FeTiO_3 polymorphs (which we found as rods parallel to [010]). Exsolution of spinels from olivine is almost invariably accompanied by a second phase, because the cations that exsolve into the spinel structure are expected to reside in

the octahedral sites of olivine; hence, precipitation of spinel leaves behind excess Si and O. The complementary phase can be a fluid (13) or a phase richer in silica than is olivine (14). In Alpe Arami, a siliceous phase is also lacking, but if Ti were incorporated in the tetrahedral site (12, 13), the reaction would be given by



where the trivalent ions in olivine are located on the octahedral sites and are compensated by vacancies, denoted by Δ . Thus, coupled substitution of trivalent cations and tetravalent Ti would result, after exsolution, in precipitation of an FeTiO_3 phase and chromite together in a molar ratio of 4:1, which is reasonably consistent with our observations (15).

The implied composition of the older generation of Alpe Arami olivine before precipitation of the oxide phases is difficult to reconcile with the strong tendency for olivine to be restricted closely to the forsterite-fayalite solid solution. Substitution of trivalent ions in the structure is a difficult process, and appreciable substitution in the tetrahedral site has not been documented.

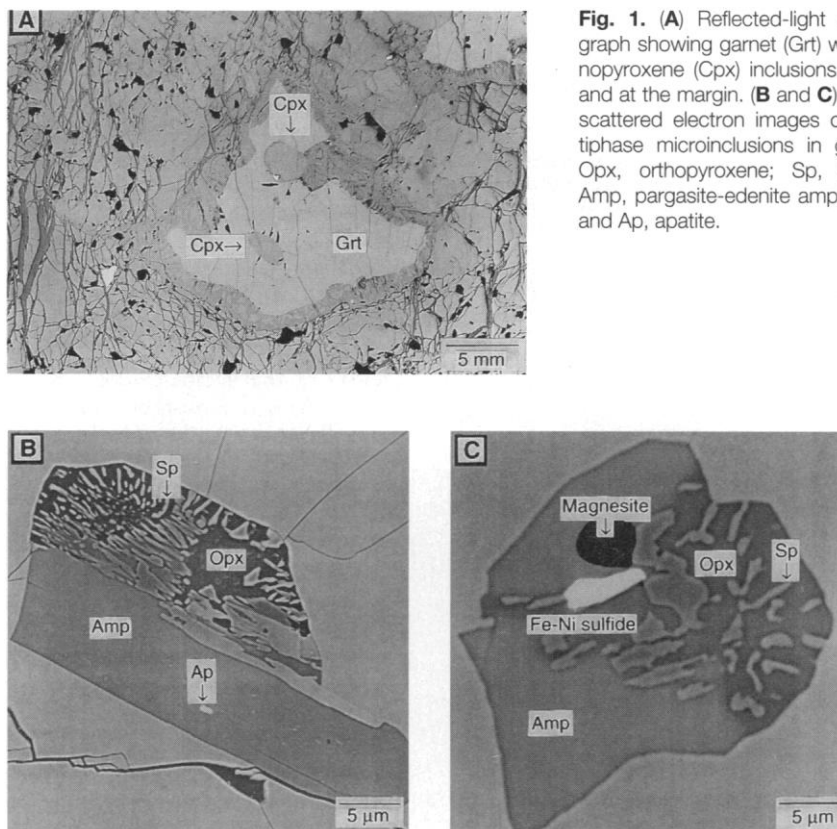


Fig. 1. (A) Reflected-light micrograph showing garnet (Grt) with clinopyroxene (Cpx) inclusions inside and at the margin. (B and C) Back-scattered electron images of multiphase microinclusions in garnet. Opx, orthopyroxene; Sp, spinel; Amp, pargasite-edenite amphibole; and Ap, apatite.

Solubility of these cations in olivine increases with depth in mantle xenoliths (10), but the concentrations found in xenolithic olivine at 250 km are distinctly less than those that were recalculated for this massif. Pressure is also known to enhance substitution of elements in the tetrahedral site of silicates. Both observations suggest that a resolution of this problem must be sought at greater depth.

Only two stable phases of FeTiO_3 are known (16)—ilmenite, which is stable under conditions obtaining in the crust and shallow upper mantle, and an orthorhombic perovskite structure that is stable at greater depths (Fig. 4). The perovskite structure does not survive decompression to atmospheric pressure, even at room temperature (16); it inverts to a metastable lithium niobate structure that resembles ilmenite, but with a different ordering scheme for Fe and Ti. We propose that the morphology and structures of the three new FeTiO_3 phases imply the former existence of the perovskite structure. This argument is based on the following observations:

1) Because ilmenite is already known to exsolve directly from olivine, there seems

little reason to conclude that the metastable phases observed here exsolved in lieu of ilmenite; some other explanation for the presence of the metastable phases must be sought.

2) Because the β phase of FeTiO_3 has almost the same unit cell as olivine, it should have the same pseudohexagonal oxygen sublattice as olivine. If so, it can be rationalized to be closely related to the lithium niobate structure, with a different ordering scheme for Fe and Ti that lacks rhombohedral symmetry (17). Such a structure would have a density $\sim 1.2\%$ greater than that of ilmenite, similar to the density of the lithium niobate structure. Thus, it is an alternative metastable inversion product of perovskite in an environment constrained by topotaxy with olivine.

3) The two phases intermediate between $\beta\text{-FeTiO}_3$ and ilmenite are both steps toward ilmenite; the first retains lattice parameters similar to a and c of olivine but halves the b parameter, whereas the second trebles the lattice parameter parallel to a of olivine. Thus, these phases are candidates for successively more stable structures [following the Ostwald Step Rule (18)], culmi-

nating in establishment of the rhombohedral symmetry during the final transformation to ilmenite (19).

4) It is reasonable to assume that the pseudocubic oxygen sublattice of the perovskite structure would have the same relation to the pseudohexagonal oxygen sublattice of olivine as is exhibited by exsolved spinel (hcp layers in common). This assumption would imply a topotaxy between the perovskite and olivine, such that $[100]_{\text{pv}} \parallel [010]_{\text{ol}}$; $[010]_{\text{pv}} \perp (10\bar{2})_{\text{ol}}$; $[001]_{\text{pv}} \perp (101)_{\text{ol}}$. The published d spacings of each of these pairs of directions are closely similar. However, despite the close agreement between olivine lattice parameters and those of all of the FeTiO_3 phases, the structures of olivine and the FeTiO_3 perovskite show the greatest mismatch across the $(100)_{\text{pv}} = (010)_{\text{ol}}$ interface; hence, this would probably

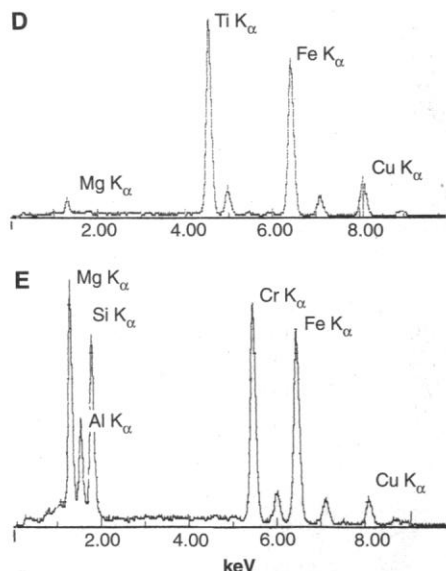
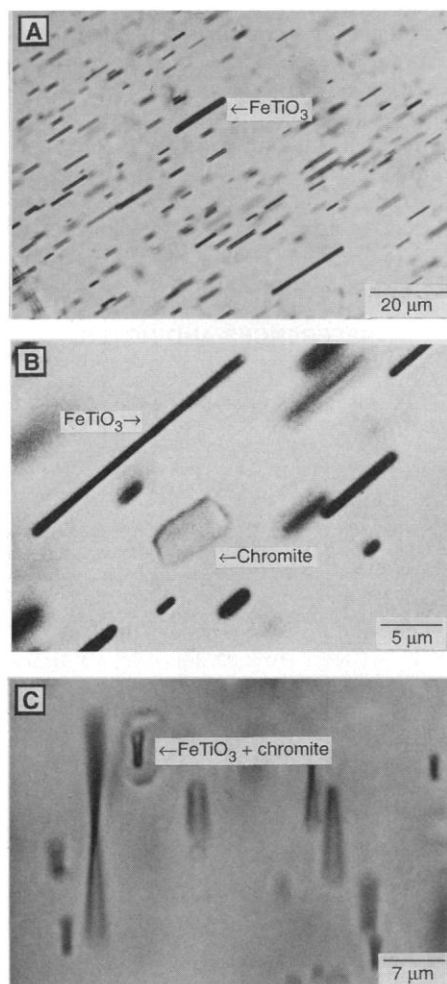


Fig. 2. Oriented ilmenite and spinel inclusions in first-generation olivine, showing exsolution morphology. (A) Low-magnification image showing the ubiquitous and dense concentration of "ilmenite" rods aligned parallel to b of olivine (at this scale, chromite tablets are difficult to recognize). (B) Chromite tablet in (100) of olivine intermixed with "ilmenite" rods. (C) Attachment of the two oxides to each other, showing parallel alignment. All images are transmitted light micrographs. (D) Energy-dispersive x-ray analysis of FeTiO_3 rods. (E) Energy-dispersive x-ray analysis of chromite tablets (Mg and Si peaks, and a small part of the Fe peak, are from the enclosing olivine). Cu peaks in (D) and (E) are from the TEM specimen grids.

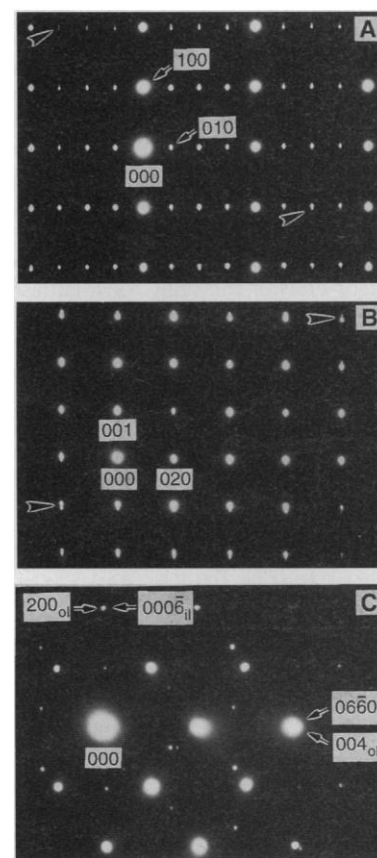


Fig. 3. Selected area electron diffraction analysis of FeTiO_3 rods. (A) Pattern for $\beta\text{-FeTiO}_3$ rod and enclosing olivine matrix, viewed down the $[001]$ olivine zone axis, showing $a_{\text{ol}} \approx a_{\beta}$; $b_{\text{ol}} \approx b_{\beta}$. Arrowheads show separation of patterns of the two phases. (B) Pattern for $\beta\text{-FeTiO}_3$ rod and enclosing olivine matrix, viewed down the $[100]$ olivine zone axis. In this zone, odd reflections (k) are missing for both phases, whereas in (A) they are not. (C) Pattern for ilmenite rod and enclosing olivine matrix, viewed down the $[010]$ olivine zone axis. In this zone, only $h + k = 2n$ reflections of olivine are permitted, and only indices $-h + k + l = 3n$ are permitted for ilmenite.

be the interface of highest energy. Minimization of energy during exsolution would result in rods of the geometry and topotaxy we observed, just as lamellar morphology can be predicted and observed in ilmenite exsolution from olivine because of the near-perfect registry of the oxygen sublattices across the $(0001)_{il} = (100)_{ol}$ plane (in both cases, such morphology minimizes interfaces with the greatest atomic misfit).

5) If the original exsolution had been to the perovskite structure, the eventual inversion of that structure to ilmenite should yield $[11\bar{2}0]_{il}/[100]_{pv}$, and hence $[11\bar{2}0]_{il}$ should be parallel to the long axis of the rods, as was observed. There is no other known reason for ilmenite to form rods in olivine with this topotaxy.

On the basis of these arguments, we conclude that (i) exsolution of the FeTiO_3 occurred as rods in the perovskite stability field, and (ii) topotactic constraints exerted by the olivine host induced metastable inversion to the $\beta\text{-FeTiO}_3$ phase during decompression instead of to the lithium niobate structure, because the latter would lead to larger coherency strains and larger interfacial energies (18). With time and continued upwelling, we postulate that many FeTiO_3 rods evolved progressively through the intermediate structures (in one case, we found different structures at different ends of the same rod), culminating in the stable ilmenite structure but retaining the rod-shaped morphology inherited from the original precipitation of perovskite (18). All of the topotactic relations between the oxide phases and olivine are consistent with this evolution.

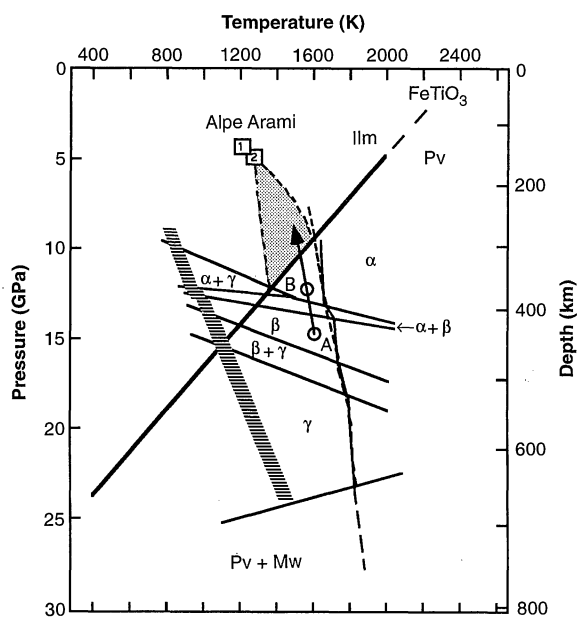
However attractive it may be, this hypothetical progression does not explain the remarkably high original solubility of highly charged cations in olivine. Similarly, it does not address the observation that the older, porphyroclastic, generation of olivine exhibits a moderate to strong LPO with [100] normal to foliation (4), whereas the recrystallized generation displays [010] subnormal to foliation with [100] subparallel to lineation (4, 7). Because the easy glide direction in olivine is [100], all natural and experimental LPOs produced by plastic flow are of the latter type (8); this pattern of LPO is responsible for the seismic anisotropy of the oceanic lithosphere (17). The former type is incompatible with such dislocation creep and is of unknown origin.

Given the extreme depth ($\geq \sim 300$ km) implied by precipitation of FeTiO_3 perovskite (Fig. 4), it is possible that the high solubility of these cations was not in olivine at all, but rather in another phase that inverted to olivine, leading to supersaturation of the highly charged cations and to their precipitation. Such a possibility also may simultaneously explain the unusual LPO of the oxide-bearing olivine as an inherited feature unrelated to olivine plasticity. Potential precursors to olivine are severely constrained by the observation that all of the oldest generation of olivine contains the oxide inclusions, and hence that any precursor phase must have had a composition such that it would have completely replaced olivine in the mineral assemblage. Two potential possibilities are that (i) the massif could have been subject to hydrous conditions at high pressure and

low temperature, with consequent replacement of olivine by phase E (20), or that (ii) the massif was sufficiently deep (>400 km) to enter the stability field of wadsleyite (β -olivine). In neither of these cases is the solubility of Ti known, but both are known to accommodate much larger amounts of trivalent cations than does olivine (15, 20). The pressure-temperature trajectory of the massif implied by the data in Fig. 4 makes the low-temperature, phase E-bearing scenario difficult to support, but is compatible with the β -olivine hypothesis. If these alternatives could explain the observed metastable phases of FeTiO_3 , they would appear to require inversion to olivine followed by exsolution of oxides, all within the stability field of FeTiO_3 perovskite (21).

These potential explanations of the observations imply different histories of the Alpe Arami massif or imply different mineralogies, depths of origin, or both. Determination that any one of them is correct will be an important contribution to our knowledge of the subduction process and of the mineralogy, volatile content, and phase chemistry of the deep upper mantle. Given that garnet peridotite has a specific gravity of >3.3 , we can envision only one mechanism for the transport of Alpe Arami to the surface: that it was carried within the surrounding Lepontine gneisses. Such a scenario requires that these continental gneisses were carried to at least 300 km by subduction, and then returned to the surface (driven by buoyancy forces after they warmed) and picked up the Alpe Arami lherzolite along the way. This model is analogous to that of von Blanckenberg and Davies (22) but requires much deeper subduction of continental rocks.

Fig. 4. Phase diagram for $(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$ and geotherms [adapted from (23)]. The thick solid curve is the temperature profile in the normal mantle derived from experimental data; the wide shaded line is the profile estimated for the coldest portions of a subducting slab. The dashed line is the theoretical geotherm from (24). Thin lines show calculated phase boundaries for α - β - γ olivine. The lowest boundary is for γ -olivine disproportionation into $(\text{Mg},\text{Fe})\text{SiO}_3$ perovskite + $(\text{Mg},\text{Fe})\text{O}$ from (25) (Mw, magnesio-wüstite). The FeTiO_3 phase boundary is from (26). Squares labeled 1 and 2 correspond to the pressure and temperature conditions for the last equilibration conditions of the Alpe Arami massif, as calculated in (5) and (6), respectively. The shaded area contains likely upwelling paths for the peridotite (the left boundary is the mantle adiabat) and indicates that the minimum depth of FeTiO_3 perovskite stability field is 300 to 400 km. The long solid arrow represents a possible upwelling path followed by the peridotite; circles along the arrow designate potential conditions of origin of the peridotite in the β -olivine stability field (circle A) and the possible position of the exsolution of FeTiO_3 perovskite rods after leaving the β -olivine field (circle B).



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31 October 1995; accepted 11 January 1996

Constraints on Rates of Granitic Magma Transport from Epidote Dissolution Kinetics

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Epidote is stable only at high pressure in granitic magmas but is found in magmas crystallized at shallow crustal levels. This observation suggests qualitatively that magma transport is sufficiently rapid to prevent complete epidote resorption. Experimental measurements of epidote dissolution showed that the presence of epidote implies that magma transport from the deep crust in these systems was rapid and that the transport was by dikes rather than diapirs.

Two different models describe the transport of granitic magma from lower crustal source regions to upper crustal emplacement sites. One model envisions magma transport occurring by diapirism (1, 2). Numerical modeling of diapirism indicates that magma transport rates are slow, ~ 0.3 m year⁻¹ up to at most ≤ 50 m year⁻¹, and ascent times are 10^4 to 10^5 years (2, 3). An alternate model favors transport by fracture propagation and dike networks; calculated magma transport rates for this process are up to 10^5 times those for diapirism (4). This correlation between the rates and mechanisms of granitic magma transport can be used to deduce the magma transport mechanism, provided that an independent estimate of transport rate is available.

Measurements of the rates of granitic magma transport are limited. Ascent rates derived for the 1980 to 1986 eruptions of Mount St. Helens dacite from depths of 8 km range from 1.4×10^5 to 2.2×10^7 m

year⁻¹ (5). Because shallow ascent is driven in part by magma vesicularity, it remains an open question whether such rates also apply to the movement of granitic magmas through the middle and lower crust.

To address this issue, we determined the dissolution rate of epidote in granitic magmas experimentally. We chose epidote for study because it has a magmatic origin in some granitic rocks (6) and its stability in granitic magmas is restricted to pressures of ≥ 600 MPa (depth of 21 km) (7). Thus, if the dissolution rate of epidote in granitic magmas at pressures of < 600 MPa is known, the presence of epidote in granites crystallized in the upper crust (200 to 300 MPa) can be used to constrain magma ascent rates from the lower crust.

In our experiments, we reacted gem quality epidote with natural granodioritic glass at pressures both above and below the stability limit of magmatic epidote (8). A high-pressure experiment (1150 MPa, 780°C, 48 hours) showed no evidence of epidote reaction with the granitic melt (Fig. 1B). We interpret this result to indicate that epidote used in our experiments is stable in granitic melt at high pressure. A time series set of experiments conducted at 750°C and 450 MPa resulted in epidote

with irregular crystal boundaries surrounded by a complex reaction rim consisting mostly of quenched melt, with minor amounts of magnetite and plagioclase (Fig. 1A). Rim widths ranged from 3 to 8 μ m; rim widths increased in longer experiments (8).

The time series data conformed to a parabolic rate law [$x = (D_{app}t)^{1/2}$], where x is the rim width, D_{app} is the apparent diffusion coefficient, and t is time (9) (Fig. 2). This relation implies that rim growth was limited by the diffusion of elements between granitic melt and epidote through the melt reaction rim. For epidote dissolution, Si, Al, Ca, and Fe are important diffusing elements, and their diffusivities in granitic melts are broadly similar (10). Using measured rim widths from our experiments (Fig. 2), we calculated a D_{app} of 5×10^{-17} m² s⁻¹ at 750°C, which is similar to a value of 7×10^{-16} m² s⁻¹ determined at 757°C in water-saturated aluminosilicate melt (9). Our results are also consistent with maximum and minimum diffusion coefficients of 1×10^{-16} and 5×10^{-17} m² s⁻¹, respectively, derived from near-solidus experiments on epidote-bearing tonalite (11). Although elemental diffusivity in granitic melts varies as a function of water content, these effects are limited for the water contents expected in natural epidote-bearing magmas (12).

Using these data, we modeled epidote dissolution in granitic magmas as a function of time, crystal size, and temperature. At 750°C, dissolution of 0.7-mm-wide epidote crystals surrounded by granite melt, for example, is complete in < 90 years; the dissolution of smaller crystals is considerably faster (Fig. 3). We extrapolated these elemental diffusivities to slightly higher and lower temperatures using measured activation energies for hydrous silicate melts (10). At temperatures appropriate for granitic magmas [700° to 800°C (13, 14)], epidote

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